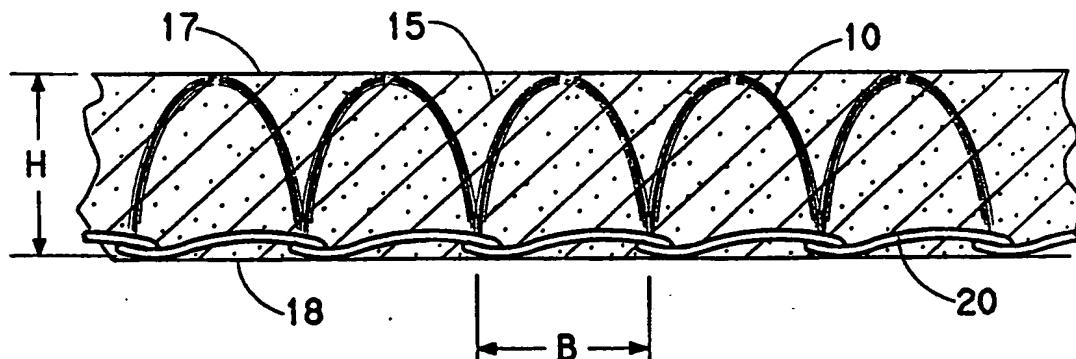




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## (54) Title: ABRASION-RESISTANT COMPOSITE SHEET



## (57) Abstract

A composite sheet having a surface layer (17) of resin-impregnated pile-like vertical fibers (10) provides the sheet with unusually high resistance to abrasive wear. The surface layer (17) has a combination of characteristics that includes an effective pile-fiber concentration of 0.1 to 0.5 g/cm<sup>3</sup>, an over-all density of at least 0.4 g/cm<sup>3</sup>, a resin content of 25 to 90 weight % and a pile parameter of at least 0.3 grams/cm<sup>3</sup>. Preferably, the pile-like fibers (10) contained within the surface layer (17) are derived from particular contracted knit fabrics or contracted two-bar stitchbonded fabrics (20).

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TITLE

Abrasion-resistant Composite Sheet

BACKGROUND OF THE INVENTIONField of the Invention

5 This invention relates to an abrasion-resistant composite sheet and to a process for making the sheet. More particularly, the invention concerns such a composite sheet in which pile-like groups of fibers are immobilized by a resin in a position that is generally vertical to the surface of the sheet.

Description of the Prior Art

10 It is known to laminate various woven or nonwoven fabrics to resin layers to form composite sheets intended for use in thermoforming and molding processes. For example, such composite sheets are disclosed in Miyagawa et al, U. S. Patent 4,298,643, Zafiroglu, U. S. Patent 5,075,142, and in Japanese Patent Application Publications 63-111050 and 63-162238.

15 Moldable composites have been utilized in many applications. However, such composites are in need of improvement when intended for use in articles that are subject to strong abrasion, for example, in athletic shoe parts, luggage surface layers, protective work clothes, heavy duty sacks, etc.

Pile fabrics and pile-like fabrics, such as velvets, velours, terry cloths, moquettes, and tufted-pile fabrics have a surface layer in which fibers are generally vertical to the surface of the fabric. Also, Zafiroglu, U. S. Patents 4,773,238 and 4,876,128, disclose certain stitchbonded fabrics in which fibrous layers are contracted by means of elastic threads to form pile-like groups of fibers. Generally, such fabrics are not disclosed for incorporation into resin-impregnated composite sheets. However, Japanese Laid-open Patent Applications 64-85614 and 64-85615 disclose a floor mat which includes a tufted-pile fabric to which a rubber resin is added. The tufted pile has an 8-mm pile height and a  $0.08\text{-g/cm}^3$  pile fiber concentration. The combination of pile fiber and resin is 62 % by weight pile fiber and 38% by weight resin. The combination has an average over-all density of 0.13  $\text{g/cm}^3$ . The mat has a pile parameter, P, as defined hereinafter, of only 0.1  $\text{g/cm}^3$ . The present inventor found that (a) such a low pile fiber concentration in combination with such a low over-all layer density and low pile parameter does not provide the mat with high abrasion resistance and (b) even if such relatively high piles are have a dense layer of resin at the outermost tips of the pile, (e.g., with all the resin in the top 1 mm of the pile) such a resin/pile layer is stretched and torn apart by strong abrasion. Increases in the abrasion resistance of such floor mats would improve their utility.

Watt et al, U. S. Patent 4,808,458, discloses flocked pile fabrics wherein a foamed resin is located primarily in the bottom 75%, preferably the bottom 50%, of the pile leaving the remainder of the pile nearly free of resin, for the purpose of obtaining a suede effect. Such products are 5 ineffective in resisting severe surface abrasion.

Zafiroglu, International Application Publication WO 94/19523 discloses an abrasion-resistant resin-impregnated nonwoven fabric. The fabric is made by contracting a nonwoven fibrous layer to cause groups of fibers buckle out of the plane of the layer and form "inverted U-shaped" 10 loops that project generally vertically from the layer and then impregnating the contracted layer with resin. Typically, within the nonwoven fibrous layer, the fibers are positioned in all directions. The individual fibers in the loops of the buckled fibrous layer therefore are not positioned in a generally perpendicular direction to the contraction, but are rather positioned in all 15 directions within the loops of the buckled nonwoven fibrous layer. Even though the groups of fibers form vertical U-shaped loops, a large fraction of the fibers within the loops still are not oriented perpendicular to the plane of the layer. Resin impregnation of such contracted fibrous layers provides a composite sheet that has an abrasion resistance that is superior to a resin-impregnated flat (not contracted or buckled) nonwoven layer, but further 20 improvements in wear resistance are desired.

An aim of the present invention is to provide a composite sheet that has a very high resistance to severe abrasive wear.

### SUMMARY OF THE INVENTION

The present invention provides an abrasion-resistant composite sheet. 25 The sheet has an upper surface and a lower surface and comprises a resin, groups of pile-like fibers and a planar fibrous network. The fibrous network is located between and substantially parallel to the upper and lower surfaces of the composite sheet. The groups of pile-like fibers are located between 30 the upper and lower surfaces and are mechanically connected to and protrude generally perpendicularly from the planar fibrous network. The composite sheet has a stretchability in any direction that is no more than 25%. The groups of pile-like fibers have an effective pile concentration,  $c_{eff}$ , of at least 0.10 g/cm<sup>3</sup>, preferably in the range of 0.15 to 0.4 g/cm<sup>3</sup>, and are surrounded 35 and immobilized by the resin in the generally perpendicular position. Typically, the resin amounts to 30 to 90 %, preferably at least 50%, of the total weight of the composite sheet. The groups of pile-like fibers and planar fibrous network are composed of fibers of textile decitex (i.e., of 0.7 to 20 dtex). Further, the pile fiber/resin layer has a thickness in the range of 0.5 to

3 mm, preferably 1 to 3 mm, an over-all density, d, of at least 0.4 g/cm<sup>3</sup>, preferably in the range of 0.5 to 1.2 g/cm<sup>3</sup>, a stretchability in any direction of no greater than 25%, preferably no greater than 10 %, a vertical compressibility of no greater than 25%, preferably no greater than 10 % and a pile parameter P, calculated by the equation,  $P = [(c_{eff})(d)]^{1/2}$ , of at least 0.3 g/cm<sup>3</sup>, preferably at least 0.35. Typically, the pile fiber/resin layer has a unit weight that is in the range of 500 to 2,500 g/m<sup>2</sup>. The surface of the composite sheet is abrasion resistant and is abraded by no more than 50 microns per 1,000 cycles of 40-grit Wyzenbeek abrasion testing.

The invention also includes a process for making the abrasion-resistant composite sheet, comprising (a) providing a fabric in which fibers form or can form pile-like fiber groups in a surface layer of 0.5-mm to 3 mm thickness in which the pile-like groups of fibers are positioned generally perpendicular to the surface of the fabric and an end of each pile-like group of fibers is mechanically attached to, or is protruding through, a generally horizontal fibrous network, (b) contracting the area of the fabric by a factor of at least two and usually not more than by a factor of 15, preferably by a factor in the range of 3 to 12, to buckle and vertically orient groups of fibers on the surface and to increase the concentration of generally perpendicular groups of pile-like fibers to a concentration of at least 0.10 g/cm<sup>3</sup>, preferably in the range of 0.15 to 0.4 g/cm<sup>3</sup>, (c) immobilizing the pile-like groups of fibers in the generally perpendicular position by incorporating a resin in the surface layer and providing the layer with an over-all density of at least 0.4 g/cm<sup>3</sup> and a pile parameter, P, of at least 0.3 g/cm<sup>3</sup>, the resin constituting in the range of 30 to 90% of the total weight of the surface layer, and (d) optionally further stabilizing the dimensions of the composite by attaching inelastic elements to the composite sheet.

The invention further provides a shaped article having the abrasion-resistant composite sheet attached to at least a portion of the surface of the article. The composite sheets provide surface layers that are capable of withstanding Wyzenbeek 40-grit abrasion-testing (as described hereinafter) with a loss in thickness of no more than 50 microns/1,000 cycles.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood by referring to the attached drawings. Figure 1 schematically represents an idealized magnified cross-section of an abrasion-resistant surface layer of the invention, in which pile-like groups of fibers are in the form of generally vertical inverted U-shaped loops 10 of height H and base B, which loops 10 are immobilized in resin 15 between upper surface 17 and lower surface 18 of the resin-impregnated

fibrous layer. The loops 10 are generally perpendicular to upper surface 17 of the layer and contracted elements 20 are generally parallel to surfaces 17 and 18. Surface 17 is the surface that is intended to be exposed to the abrasive conditions. Fig. 2 represents a segment 11, of a yarn or of a bundle of fibers in a nonwoven fibrous layer, before buckling or contraction of the 5 yarn or layer, the segment being located between stitches or fixed points 12 and 13, which are a distance of S apart. Fig. 3 and 4 respectively represent segment 11 would appear after the fabric or fibrous layer in which it was located is contracted by a factor of two (Fig. 2) or three (Fig. 3) in the 10 direction of the length of the segment. Note that the greater contraction is accompanied by a greater verticality of the fiber bundles or yarns.

#### **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

The following description of preferred embodiments is included for the purposes of illustration and is not intended to limit the scope of the 15 invention; the scope is defined by the appended claims.

As used herein, the terms "pile-like groups of fibers" or "pile-like fibers" includes buckled yarns, inverted-U-shaped loops formed from buckled nonwoven layers of textile fibers, tufted yarns and the like. The fibers within each of these pile-like groups of fibers, as well as the fibers of 20 the nonwoven fibrous layers, are of conventional textile decitex, namely, of 0.7 to 20 decitex.

The highly abrasion-resistant composite of the invention has a surface layer in which pile-like groups of fibers are crowded together and immobilized by a resin within the surface layer. The pile-like fibers protrude 25 generally perpendicularly from a fibrous network that is also located within the surface layer, for example at the mid-plane or at the base of the layer. The fibrous network can be a nonwoven fibrous layer, a knitted fabric, a woven fabric, or the like. Typically, as shown in Fig. 1, the fibrous network 20 is located no further than 3 mm from outer surface 17 of the layer that is to be exposed to abrasion. The resin 15 and the fibrous network 20 prevent 30 the pile-like fibers 10 from moving from side to side or from collapsing into the layer when the surface of the composite is subjected to lateral and normal forces during repeated cycles of abrasion or rubbing. The composite has a stretchability and the resin/pile-fiber layer has a compressibility (measured 35 as described hereinafter), each of which is no greater than 25%, preferably no greater than 10%. Stretchability and compressibility, respectively are measures of how much the fibers can be moved from side to side and how much the fibers can be collapsed from their perpendicular position when the composite is subjected to conditions of severe abrasion.

In accordance with the invention, the surface layer of the abrasion-resistant composite has a thickness in the range of 0.5 to 3 mm. Thicknesses of greater than 3 mm are avoided because it is difficult to immobilize and stabilize pile-like layers if the to-be-abraded surface is further than 3 mm away from the horizontal fibrous network. The effective concentration,  $c_{eff}$ , of the generally vertical pile-like fibers within the surface layer is in the range of 0.1 to 0.5 gram/cm<sup>3</sup>, preferably in the range of 0.15 to 0.4 g/cm<sup>3</sup>. In the surface layer of the composite, the resin constitutes 30% to 90%, preferably at least 50% and most preferably at least 70%, of the total weight of the layer. The over-all density,  $d$ , of the surface layer is at least 0.4 g/cm<sup>3</sup>. For high resistance to abrasion and wear, the surface layer of the composite has a "pile parameter",  $P$ , that is at least 0.3 g/cm<sup>3</sup>. The pile parameter,  $P$ , as defined herein is the square root of the product of the pile-like fiber concentration and the overall density of the surface layer. The pile parameter is expressed by the formula,  $P = [(c)(d)]^{1/2}$ .

Typically, the surface layer of a composite sheet of the invention is not completely filled with resin and fiber. The layer can contain many small voids. An over-all density of the surface layer of at least 0.4 g/cm<sup>3</sup>, and generally not more than about 0.9 g/cm<sup>3</sup>, automatically implies the presence of voids in the surface layer amounting to at least 10% and as much as 65% or more of the total volume of the layer, because most fibers and resins suitable for use in the invention have densities of at least 1.0 g/cm<sup>3</sup>. However, overall densities of as high as 1.2 g/cm<sup>3</sup>, and accordingly resin densities of greater than 1.0 g/cm<sup>3</sup> are contemplated for use in the invention. For lighter weight and more flexible composite sheets, surface layer void volumes of 25 to 75% are preferred. Usually, high amounts of resin are employed in the composites that have low concentrations of vertical fibers in the surface layer. For example, in composite sheets of the invention having effective pile-fiber concentrations near the lower 0.1-g/cm<sup>3</sup> limit, a layer constituting 70 to 90% resin is preferred. For relatively high effective pile-fiber concentrations, lower percentages of resin can be used (e.g., 30-50%).

Various types of resins are suitable for immobilizing the fibers or fiber bundles in the generally vertical position. Particularly useful polymeric resins include polyurethanes, epoxies, synthetic rubbers, polyesters, polyacrylates, polyethers, polyetheresters, polyamides, copolymers and mixtures thereof and the like. The resins can be thermoplastic or thermosetting. Very soft resins, for example soft rubber latexes or resins that are highly foamed, generally are not suitable for use in the present invention. Resins suitable for use in the invention adhere well to the fibers and usually

are well distributed throughout the pile-fiber layer. However, if the resin distribution is not fully uniformly distributed throughout the pile-fiber layer, the resin preferably is concentrated nearer the surface that is to be abraded than to the end mechanically attached to the horizontal fibrous network.

5       The resins can be applied to the pile-fiber layer in any of several conventional ways, as for example, by dipping, spraying, calendering, applying with a doctor knife, or other such techniques. The resin may be applied from a solution, dispersion or slurry or by melting a layer of the resin and forcing it into the layer of vertical fibers. The resin also can be.

10      introduced as adhesive particles or as binder fibers that are activated by heat or chemicals. Conventional coagulation and/or foaming techniques also may be employed in applying the resin. In most instances, the resin or binder can be introduced into the fibrous layer before, during or after the contraction step which is required according to the process of the invention for obtaining

15      the desired density of vertical fibers in the surface layer. However, when forming the surface layer and incorporating resin, care must be taken to avoid deflecting the fibers from their vertical position and to avoid immobilizing the fibers before the fibers have been positioned vertically. After incorporation into the pile-like fiber layer, the resin is dried and/or

20      cured by conventional methods. If during resin application, the pile-like fiber layer is compressed in thickness by as little as 25%, the pile-like fibers sometimes can be deflected significantly from verticality and result in the composite sheet having decreased abrasion resistance.

25      The surface layer of a composite sheet of the invention is much more abrasion resistant than a 100% resin layer containing no vertical fibers or a resin/fiber surface layer in which the fibers are not in a vertical position. For example, composites of the invention having vertical fibers encased in a layer of relatively soft polyurethane resin can be 50 to 150 times more resistant to abrasion than a layer made from 100% of the same resin. When

30      harder, relatively more wear-resistant resins are employed, the advantage of the fiber/resin layer of the invention over a layer of 100% of the same resin is not as great. However, compared to surface layers containing no fibers or containing primarily horizontal fibers, surface layers of composites of the invention still are very much more abrasion resistant.

35      In the process of the invention, the first step provides a fabric that has, or has the capability of forming, a pile-like fiber layer. As used herein, the term "pile-like fiber layer" means a surface layer of a fabric within which fibers are positioned generally vertical to the surface of the fabric.

In accordance with certain embodiments of the process of the invention, the generally vertical fiber layer is derived from a substantially nonbonded fibrous nonwoven layer which is subjected to a contraction step that causes fibers or groups of fibers to buckle out of the flat plane of the fibrous nonwoven fabric to form the pile-like layer. The generally vertical fibers of the pile-like layer are depicted in Figure 1 and often appear as inverted U-shaped loops, of height H and base B. Such loops, when formed in part from a nonbonded fibrous nonwoven, typically have an average spacing (i.e., base B) in the range of 0.1 to 2 mm, and a height-to-base ratio of at least 0.5. Loop spacings as small as 0.1 mm and height to base ratios of as large as 15 can be achieved when the layer is highly contracted (e.g., by a factor of 10 to 15) and additional elements capable of forming pile or pile-like fibers are included in the structure (e.g., other non-elastic yarns in the stitching patterns). Practical ways to determine the H and B dimensions of the loops, are described below in the paragraphs on test methods.

A typical nonwoven fibrous layer for use in an embodiment of the process of the invention is a thin, supple, substantially nonbonded web of staple fibers or continuous filaments of textile decitex. These fibrous materials are referred to collectively herein as "fibers". The fibers are naturally occurring or formed from synthetic organic polymers. Fibers that are smaller than 5 dtex and longer than 5-mm are preferred. Preferred fibrous layers are capable of buckling over a relatively short interval (e.g., as small as 1 mm) and typically weigh in the range of 15 to 100 grams/square meter, preferably less than 60 g/m<sup>2</sup>. Suitable materials for the starting nonwoven fibrous layer include carded webs, air-laid webs, wet-laid webs, spunlaced fabrics, spunbonded sheets, and the like. Generally, thick lofty webs, felts, adhesively or thermally bonded webs, or the like are not suitable; such materials usually are difficult to buckle over short intervals.

Contraction and buckling of the fibrous layer can be accomplished in any of several ways. For example, a contractile element, or array of contractile elements, can be intermittently attached to the fibrous layer. The spacing between attachment locations is typically at least 1 mm to allow for efficient buckling. Then, the element or array of elements is caused to contract so that the area of the fibrous layer is decreased significantly and groups of fibers buckle out of the plane of the layer. Before the contractile elements are attached, additional gathering or contraction can be imparted to the fibrous starting layer by overfeeding the layer to the apparatus being employed to attach the contractile elements.

Many types of contractile elements are suitable for use in the present invention. For example, the nonwoven fibrous layer can be stitchbonded with elastic yarns under tension. Textured stretch yarns, covered or bare spandex yarns and the like are suitable yarns for contractile element stitching. After the stitching, the tension can be released to cause the desired contraction and buckling of the fibrous layer. Instead of stitching, extended elastic elements in the form of warps, cross warps, films or the like, can be intermittently attached to the fibrous layer by hydraulic entanglement, adhesive or thermal point bonding, or the like. Thereafter, tension on the extended elements can be released to cause layer contraction and buckling.

Other types of contractile elements, which shrink on being treated with heat, moisture, chemicals or the like can be attached intermittently to the fibrous layer without initial tension or extension in the elements. After attachment, the contraction of the contractile elements can be activated by appropriate treatment.

Still another way of accomplishing the contraction and buckling of the fibrous layer involves intermittently attaching the fibrous layer to a stretchable substrate that necks-in in a direction that is transverse to the direction in which the substrate is pulled. For example, certain substrates, when stretched by 15% in one direction, can automatically experience substantially irreversible contraction (i.e., neck in) in the transverse direction by an amount that is two or three times the amount of stretch. Thus, appropriate intermittent attachment of a fibrous layer to the stretchable substrate before the stretching and necking-in operation, and then applying the stretching forces to the combined layer and substrate, can significantly decrease the area of the fibrous layer and cause buckling of groups of fibers as required by the process of the invention.

In other embodiments of the invention, the pile-like layer of fibers is derived from conventional yarns in a knit or woven fabric which is constructed with contractile elements. When the contractile elements contract, the area of the fabric decreases significantly and causes the conventional yarns of the fabric to gather and buckle and project in a vertical direction from the horizontal plane of the gathered fabric. In another embodiment, the pile-like layer includes loops of fibers that project from wrapping yarns that were loosely wrapped around the axis of the contractile core of an elastic combination yarn. Generally, yarns that can be contracted and buckled provide denser pile-like layers than do contracted and buckled nonwoven fibrous layers. After resin is applied according to the invention,

the resultant composite sheets made with buckled yarns possess a higher abrasion resistance than those made with buckled nonwoven fibrous layers.

In still other embodiments of the invention, a pile-like layer can be derived from a combination of a contracted substantially nonbonded fibrous nonwoven fabric, loose wrapping yarns of a contracted combination yarn and/or a buckled non-elastic yarn. In those embodiments wherein the pile-like layer is formed partially or totally from buckled yarns derived from a knit or woven fabric, the knit or weave is sufficiently coarse to permit satisfactory yarn buckling. Typically, the buckled elements, before buckling, have a flat length of at least 1 mm. In yet another embodiment of the invention, a tufted pile fabric is contracted to increase the density of the pile tufts, for use in a composite sheet of the present invention.

As used herein, a combination yarn means a yarn having a contractible core (e.g., provided by an elastic or shrinkable yarn) surrounded by a non-contractible conventional "wrapping" yarn or "covering" yarn. The wrapping or covering yarn may be of any natural or synthetic fiber. The wrapping may be combined with the elastic core while the elastic core is under tension by conventional wrapping, winding, plying, covering, air jet entangling or intermingling, or the like. The core may be a yarn or monofilament of any elastic material. Cores of spandex yarn are preferred. If the wrapping yarn is combined loosely (e.g., fewer than 3 turns/inch) with a tensioned and extended elastic core, when the tension is released, the core contracts and the wrapping yarn contracts and buckles perpendicular to the core. When a fabric is knit, woven or stitchbonded with a combination yarn under tension, when the tension is released from the combination yarn, the yarn contracts and the wrapping yarn buckles contributing pile-like fibers to the surface layer. However, if the wrapping yarn is wound too tightly around the elastic core, the combination yarn cannot provide pile-like fibers to the composite sheet

In the contraction step of the process of the invention, the area of the fabric from which the vertical fibers are derived is contracted by a factor of at least 2, preferably in the range of 3 to 10 and sometimes by a factor as high as 15. The contraction step is employed before or during application of the resin. The fabric cannot be contracted after the resin has become set.

As a result of the contraction step, the concentration of vertical pile-like fibers in the surface layer of the fabric is significantly increased. Then, the fibers are immobilized in place by adding a resin to the surface layer, in an amount in the range of 30 to 90% of the total weight of the resin-containing layer (i.e., weight of resin and pile-like fibers). Preferably the

resin amounts to at least 50% and most preferably at least 70% of the total weight of the layer. Typically, the resin is distributed uniformly throughout the layer of pile-like fibers. However, as long as the pile-like fibers are immobilized in a substantially vertical position, the distribution of resin can be somewhat non-uniform and there also can be a fairly large void fraction in the layer. The voids can amount to as much as 75% or more of the total volume of the layer. Ridding the layer of voids to completely fill the layer with resin is unnecessary. In fact, techniques for this purpose are avoided because the techniques often excessively crush the fibers and deflect the fibers from a vertical position. Vertical pile-like fibers in the resin/fiber layer are essential for the improvements in abrasion resistance provided by the composite sheets of the invention.

In addition to the pile-like fabrics described above, composite sheets according to the invention also can be produced from other types of pile fabrics, such as tufted pile fabrics, velvets, moquettes, and velours so long as the fabrics have a pile height and a pile fiber concentration within the requirements of the present invention and the fabrics are capable of being combined with resin to produce a layer having a pile parameter of at least 0.3 g/cm<sup>3</sup>. Such starting fabrics typically have pile-fiber concentrations in the range of 0.05 to 0.15 g/cm<sup>3</sup>. In composite sheets made with such fabrics, the resin typically amounts to at least two-thirds of the total weight of the pile-like fiber/resin surface layer. The over-all density of the pile-like fiber/resin layer is generally at least 0.4 g/cm<sup>3</sup>, preferably in the range of 0.5 to 0.9 g/cm<sup>3</sup>. Higher, rather than lower, pile densities are preferred because the higher density piles are more resistant to compression and pile fiber deflection during the resin- impregnation step and ultimately can lead to a more abrasion resistant layer.

The abrasion-resistant surface of the composite sheet of the invention is resistant to lateral stretch, and to vertical compression. The stretchability and compressibility of the composite sheet can be controlled in several ways. The stretchability of the composite sheet is affected greatly by the horizontal fibrous network to which the pile-like fibers are attached and from which the pile-like fibers protrude. An inherently non-stretchable fiber network, located within about 3 mm of the outer surface of the composite, can impart non-stretchability to the resin-fiber surface layer. For low stretchability and low compressibility, a hard resin, rather than a softer one, is preferred. Lateral stability of the composite sheet in any linear direction also can be achieved by the attachment of strong, substantially non-stretchable strips, films, sheets, webs, cross-warps or the like to the back surface of the

abrasion-resistant layer. The attachment may be made by any convenient means, such as gluing, thermal bonding or the like.

Abrasion-resistant composite sheets of the invention are suitable for use in many different articles. The sheets can be molded into various shaped articles, can be used as single or multiple layers, or can be attached by various means to the surface or portions of the surface of various shaped articles to provide the articles with abrasion resistance. For example, composite sheets of the invention are suited for use in shoe uppers, work gloves, automotive engine timing belts, leather-like apparel, indoor athletic protective pads, women's pocketbooks, bags, luggage, saddles, seating surfaces, etc. The more abrasion-resistant composite sheets of the invention are especially suited for articles that are subjected to more demanding abrasion conditions, such as toe, heel and/or sole portions of shoes, bottoms of industrial bags that are often dragged on concrete floors, bearing surfaces of interacting mechanical parts, soccer balls, heavy duty work boots, gloves, motor-cyclist apparel pads, and the like.

#### Test Methods

The following methods and procedures are used to measure various characteristics of the resin-impregnated fabrics of the invention.

In composite sheets of the invention, which have vertical pile-like fibers formed by the buckling of a nonwoven fibrous layer or by the buckling of yarn segments over short intervals, inverted U-shaped loops are formed from buckled groups of fibers or from buckled yarns. The height H and the base B of the U-shaped loops of buckled groups of fibers are determined from magnified (e.g., 15-20X) photomicrographs of cross-sections of the loops taken through the loops in a plane perpendicular to the plane of the fibrous layer. The data are then used to calculate an H/B ratio. A low magnification microscope with strong top and/or back lighting on the sample permit direct measurement of H and B. Usually the average loop height H is equal to the thickness of the contracted fibrous layer. Alternatively, the average loop height H can be measured directly with a "touch" micrometer having a 1/4-inch (0.64-cm) diameter flat cylindrical probe which applies a 10-gram load to the contacted surface. A digital micrometer, model APB-1D, manufactured by Mitutoyo of Japan is convenient for the measurement.

In addition to the above-described method, "verticality" of pile-like fibers can be determined by examination of a magnified cross-section of the fiber/resin layer. If loops are "crushed" or excessively "pushed down" during resin application, a relatively long flat portion of the inverted U is seen near the outer surface of the fiber/resin layer. Deflection of straight

fibers or yarns from a vertical position also is readily observable. Such severe deflection of pile fibers can occur during resin application. A 30% decrease in pile-fiber layer thickness during resin application can decrease the abrasion resistance of the final composite sheet, especially when the pile fiber concentration is near the lower end of the range of concentrations suitable for use in the present invention.

Stretchability, S, is determined by: (a) cutting a specimen measuring 2-cm wide by 10-cm long sample from the composite sheet; (b) marking a standard length,  $L_0$ , on the specimen parallel to the long dimension; (c) suspending a 1.0-kilogram weight from specimen for 2 minutes; (d) with the weight suspended, re-measuring the "standard length", the re-measured length being designated  $L_f$ , and (e) calculating the percent stretchability, %S, by the formula,  $\%S = 100 (L_f - L_0)/L_0$ .

Compressibility, C, is determined by measuring the change in thickness of the surface pile-fiber/resin layer of the composite sheet (a) under no pressure,  $t_0$ , and (b) under a pressure of 351 kiloPascals ( $51 \text{ lb/in}^2$ ),  $t_f$ . A thickness gage is employed which imparts a 2.5-pound (1.14-Kg) load onto the pile fiber/resin composite through a cylindrical foot of 1/4-inch (0.64-cm) diameter. Then, the percent compressibility, %C, is calculated by the formula,  $\%C = 100 (t_0 - t_f)/t_0$ . To avoid possible errors in these determinations, caused by the presence of a compressible horizontal fibrous network within the impregnated layer and to assure that it is the characteristics of the pile fiber/resin layer that are being measured, the horizontal fibrous network is carefully removed by sanding until only the pile/resin layer remains.

The unit weight of a fabric or fibrous layer is measured according to ASTM Method D 3776-79. The density of the resin-impregnated fabric is determined from its unit weight and its measured thickness. The void fraction of the layer can be readily determined from the measurements of the over-all density of the layer and the weights and densities of the fiber and resin in the layer.

Over-feed ratio, contraction ratio and total gather are parameters reported herein which are measures of how much an initial fibrous layer contracts or gathers as a result of the operations to which the layer is subjected. The over-feed ratio, which applies only to the embodiments of the invention which employ a buckled nonwoven fibrous layer, is defined as the ratio of the initial area of a starting fibrous nonwoven layer to the area of the layer immediately up-stream of a first processing step (e.g., a stitchbonding step). Over-feed causes buckling, gathering or compression of

the nonwoven layer in the direction in which it is being fed to the operation. The contraction ratio is a measure of the amount of further contraction the nonwoven layer undergoes as a result of the specific operation to which it is subjected (e.g., stitchbonding and release of tension from yarns to which the fibrous layer was intermittently attached). The contraction ratio is defined as the area of the fibrous layer as it enters the specific operation divided by the area of the fibrous layer as it leaves the specific operation. The total gather is defined as the product of the over-feed and contraction ratios. The fraction of original area is the reciprocal of the total gather and is equivalent to the ratio of the final area of the fibrous layer to the initial area of the starting fibrous layer.

The effective pile fiber concentration is determined from the concentration of fibers within the surface layer of the composite sheet which are in a vertical (or pile-like) position with respect to the surface that is to be exposed to abrasion. For fabrics in which the pile-like fibers are derived from buckled hard yarns (e.g., as in a contracted knit fabric) the effective pile fiber concentration is the weight of the hard yarns in a unit of area divided by the thickness of the layer. Similarly, if the pile-like yarns are provided by buckled yarns that had been loosely wrapped around a stretched elastic yarn that had then been permitted to contract, the total weight of the wrapping yarns are included in the calculating the concentration of the pile yarns, but the weight of the elastic core is not included. For composite sheets in which the pile-like yarns are formed from a contracted-and-buckled nonwoven fibrous layer, only 50% of the weight of the nonwoven fibrous layer is included in the calculation of the pile-fiber concentration. The present inventor found empirically, that the abrasion-resistance-versus-pile-parameter data for composites of the invention correlate much better when only half the weight of the buckled nonwoven fibrous layer is employed rather than the full weight said layer. This reflects the fact that pile-like fibers formed from buckled hard yarns and tufted pile fibers, for example, are more effective in providing abrasion resistance to the composite sheet than are pile-like fibers formed from contracted-and-buckled nonwoven fibrous layer. Thus, the effective pile fiber concentration,  $c_{eff} = 10^{-4} kw/t$ , wherein k is 0.5 for pile-like fibers provided by buckled nonwoven fibrous layers and 1.0 for buckled yarns or tufts, w is the unit weight of the pile-like yarns in grams per square meter and t is the thickness of the surface layer in centimeters.

To determine the abrasion resistance of samples a Wyzenbeek "Precision Wear Test Meter", manufactured by J. K. Technologies Inc. of

Kankakee, Illinois, is employed with a 40 grit emery cloth wrapped around the oscillating drum of the tester. The drum is oscillated back and forth across the face of the sample at 90 cycles per minute under a load of six pounds (2.7 Kg). The test is conducted in accordance with the general procedures of ASTM D 4157-82. The thickness of the sample is measured with the aforementioned thickness gage before and after a given number of abrasion cycles to determine the wear rate in microns lost per 1,000 cycles. To provide adequate wear resistance to the composite sheets of the invention, a wear rate of no more than 50 microns/1000 cycles is considered 10 to be satisfactory.

#### EXAMPLES

In the following Examples, the fabrication and abrasion resistance of various composite sheets of the invention are illustrated and compared to similar composite sheets that are outside the invention. The composite 15 sheets of the invention are much more abrasion resistant than are the comparison composite sheets. Samples of the invention are designated with Arabic numerals and comparison samples with upper case letters. Conventional warp-knitting nomenclature is used to describe the particular repeating stitch patterns that were employed to prepare the various knit or 20 stitchbonded fabrics of the Examples. A table accompanies each example and records fabrication details, weights, composition and characteristics of each composite sheet, as well as the abrasion performance of the sheet.

In the examples, fabrics that were made with elastic yarns were in sequence (1) removed from the fabric forming machine, (2) allowed to 25 achieve an initial contraction, (3) subjected to a "boil-off" treatment by being immersed in boiling water (100°C) for 1-2 minutes, (4) dried and then (5) heat set on a tenter frame for 1-1.5 minutes at 380°F (193°C). The particular amounts of stretching in the longitudinal and transverse directions during the heat setting were used control the final amount of contraction experienced by 30 the fabric.

Two different polyurethane resins were used for impregnating the pile-like layer of the composite samples. "ZAR", a clear polyurethane finish sold by United Gilsonite Laboratories of Scranton, Pennsylvania, designated herein as "PU-1", was used for the samples of Examples 1 and 3. PU-2, a 35 softer polyurethane resin, sold by K. J. Quinn & Co., Inc. of Seabrook, New Hampshire was used for all the remaining samples. PU-2 is a two-part formulation that was mixed, applied to the pile fibers and then cured. The samples were resin-impregnated by conventional dipping techniques. The applied resin was smoothed with a doctor blade and dried and/or cured with

the pile fibers facing downward for at least 12 hours in a hot-air oven. Oven temperature was maintained at 65°C for fabrics impregnated with PU-1 and at 95°C for fabrics impregnated with PU-2. The compressibility, density and 40-grit abrasion wear rates (in microns/1000 cycles) and Shore A hardness of a 5-mm-thick layer of each resin containing no fibers were as follows:

<u>Resin</u>	<u>Shore A hardness</u>	<u>% Com- pressibility</u>	<u>Density g/cm<sup>3</sup></u>	<u>Abrasion wear rate</u>
PU-1	70	0	1.1	900
PU-2	53	5	1.0	4,500

10      **Example 1**

This example compares two samples of resin-impregnated composite sheets of the invention with a sample that is outside the invention. In each sample, pile-like fibers are formed of Kevlar® aramid fibers (sold by E. I. du Pont de Nemours & Co.). In Sample 1, the pile-like fibers are formed by the buckling of Kevlar® yarns in a knit fabric. In Sample 2, the pile-like fibers are formed from buckled Kevlar® stitching yarns and a buckled nonwoven fibrous substrate of Kevlar® in a stitchbonded fabric. In comparison Sample A, which is outside the invention because of its low effective pile-fiber concentration and low pile parameter, the pile-like groups of fibers are formed only from a buckled nonwoven layer of Kevlar® fibers. Samples 1 and 2 the invention are shown have between about 3 to 5 times the abrasion resistance of comparison Sample A.

The starting fabric for the composite sheet of Sample 1 was a two bar knit fabric that was prepared with a "Liba" machine operating at 10 gauge (10 rows per inch or 4 per cm) and 22 courses per inch (8.7 per cm). The back bar was threaded with 400 den (440 dtex) filament Kevlar®-29 yarn forming a repeating pattern of 1-0,4-5 stitches. The front bar was threaded with a combination yarn that consisted of a 280-den (320-dtex) Lycra® spandex elastic core, around which was tightly wound, at about 7 turns/inch (2.8/cm), a 70-den (78-dtex) 34-filament textured polyester yarn. Upon removal of the knit fabric from the LIBA machine, the as-knit fabric weighed 159 g/m<sup>2</sup>. The as-knit fabric was then boiled-off and heat set. As a result the fabric contracted by a factor of 2.6 and increased its weight to 413 g/m<sup>2</sup>. The back bar yarn buckled to form groups of inverted U-shaped pile-like fibers. The tight wrapping of the combination yarn of the front bar yarn did not contribute to the formation of pile-like groups of fibers. Then, the fabric was impregnated with polyurethane resin PU-1 and dried and cured in the hot-air oven. Characteristics of the resultant composite sheet, Sample 1, are recorded in Table I below.

The starting fabric for the composite sheet of Sample 2 was a two-bar stitchbonded fabric that was prepared with a 140-inch (3.6-meter) wide, two-bar "Liba" machine adapted for stitchbonding a nonwoven fibrous layer. Each bar was threaded to 14 gage (14 rows/inch or 5.5/cm) and inserted 9 stitches per inch (3.5/cm) in each row. A 34-g/m<sup>2</sup> Type Z-11 Sontara® spunlaced fibrous substrate (made by E. I. du Pont de Nemours & Co.) of Kevlar® 29 aramid fibers of 1.5 den (1.7 dtex) per filament and 2.2 cm length was fed to the LIBA with 47% overfeed. The back-bar and front-bar stitching threads were the same as those used for Sample 1, but formed opposing 2-course Atlas stitch patterns. Upon removal of the stitchbonded fabric from the LIBA, the fabric contracted in area and increased its weight to 184 g/m<sup>2</sup>. The stitchbonded fabric was then boiled off, heat set and resin impregnated in the same manner as for Sample 1, except that the area of Sample 2 in the boiling and heat setting contracted by a factor of 2.9 and the nonwoven fibrous layer, which had been overfed to the stitchbonding step, experienced a total gather of 4.3. Further details of the fabrication and characteristics of Sample 2 are listed in Table I below.

A comparison composite sheet, Sample A, was prepared from the same type and weight of Kevlar® spunlaced starting fabric as was used for Sample 2. A one-bar stitchbonding machine, threaded at 12 gauge (12 needles /inch or 4.7/cm) and inserting 14 stitches/inch (5.5/cm), was used for Comparison Sample A. The nonwoven fibrous layer was overfed 25% and stitched with the same combination yarn as was used in preparing Samples 1 and 2. A 1-0, 2-3 repeating stitch pattern was employed. Sample A was resin impregnated, boiled off and heat set in the same way as Samples 1 and 2. Details of comparison Sample A are summarized in Table I.

The data of Table I clearly demonstrate the superior abrasion resistance of composite sheet Samples 1 and 2 over comparison composite sheet of comparison Sample A. Samples 1 and 2 respectively were 2.7 and 3.1 times as abrasive resistant as the comparison Sample A.

Table I (Example 1)

Sample Identification		1	2	A
<b>Starting Materials</b>				
	Nonwoven wt., g/m <sup>2</sup>	0	34	34
5	Over-feed ratio	na	1.47	1.25
	Hard yarns wt., g/m <sup>2</sup>	135	104	0
	Contractibles wt., g/m <sup>2</sup>	24	30	44
	Total wt., g/m <sup>2</sup>	159	184	87
<b>Gathering</b>				
10	Contracted wt., g/m <sup>2</sup>	413	537	361
	Contraction ratio	2.6	2.9	4.15
	Nonwoven wt., g/m <sup>2</sup>	0	145	176
	Hard yarn wt., g/m <sup>2</sup>	351	302	0
	Nonwoven total gather	na	4.3	5.2
15	% of original area	38	35	24
<b>Resin application</b>				
	Resin wt., g/m <sup>2</sup>	306	566	510
	% pile height loss	0	0	0
<b>Surface layer characteristics</b>				
20	Total wt., g/m <sup>2</sup>	657	1013	686
	Thickness, mm	1.1	2.0	1.4
	Density, g/cm <sup>3</sup>	0.59	0.51	0.49
	Pile fiber weight, g/m <sup>2</sup>	351	445	176
	Pile fiber conc., g/cm <sup>3</sup>	0.32	0.23	0.13
25	Effective pile conc., g/cm <sup>3</sup>	0.32	0.19	0.065
	Pile Parameter, P, g/cm <sup>3</sup>	0.44	0.32	0.18
	Loop base, B, mm	0.7	0.5	0.4
	Loop H/B ratio	3.6	5.0	3.5
	Wt. % resin	46	56	74
30	% voids	51	58	59
	% stretchability	10	10	10
	% compressibility	10	10	5
<b>40-grit abrasion resistance</b>				
	Test duration, 10 <sup>3</sup> cycles	>5	>5	>5
35	Wear, microns/10 <sup>3</sup> cycles	23	36	110
	% normalized wear*	21	33	100

Note: na = not applicable; \* = Normalized to Sample A.

**Example 2**

In this example, several samples of composite sheets of the invention and comparison samples similar to those of Example 1 are prepared, but with softer polyurethane resin PU-2 replacing polyurethane resin PU-1 of Example 1. Each sample and comparison sample has groups of pile-like fibers formed from Kevlar® aramid fibers.

Sample 3, Sample 4 and comparison Sample E, respectively, contain the same fabrics as Samples 1 and 2 and comparison Sample A of Example 1. The composite sheet of Sample 3 includes a contracted fabric that had been knit with an elastic combination yarn on one bar and a non-elastic yarn on the second bar. The composite sheet of Sample 4 includes a contracted fabric that had been prepared by stitchbonding a fibrous layer with one bar of elastic composite yarn and one bar of non-elastic yarn. Sample E includes a contracted fibrous layer that had been prepared by stitchbonding the layer with a single bar of elastic combination yarn. Additional composite sheet comparison Samples B and C respectively are made with the same starting fabrics as Samples 3 and 4, but with different amounts of resin applied. Further details on the fabrication, characteristics and abrasion performance of the resultant composite sheet samples are summarized in Table II. Table II clearly shows the abrasion-resistance advantage of composite sheets made with pile parameters of high value. See for example, the abrasion-test results for Sample 3 versus comparison Sample B and Sample 4 versus comparison Sample C. Also, the abrasion wear results for these samples, and Sample E, versus of the corresponding samples in Example 1 show that as long as the resins immobilize the fibers and provide low compressibility and stretchability to the layer, increasing resin hardness apparently does not increase abrasion resistance of the composites of the invention. Increases in pile-fiber concentration and pile parameter are more effective.

In addition to the above-described composite sheets containing fabrics with pile-like groups of Kevlar® aramid fibers, two more composite sheets, Sample 5 and comparison Sample D, are prepared. Starting fabrics for these two samples are made by tufting a 1,000 den (1,100 dtex) Kevlar®-29 yarn into a 119-g/m<sup>2</sup> lightly bonded Reemay® spunbonded polyester nonwoven fabric (made by Reemay, Inc., of Old Hickory, Tenn.) at 16 tufts per inch (5.1/cm) at 14 gauge (14 tufting needles per inch or 5.5/cm). The tufted fabric was stretched 20%, with an accompanying necking-in of about 40%, to contract the area of the fabric by a factor of 2. Further details of the composite sheet construction and performance are summarized in Table II.

Table II (Example 2)

Sample Identification		3	B	4	C	5	D	E
<b>Starting Materials</b>								
	Nonwoven wt., g/m <sup>2</sup>	0	0	34	34	119	119	34
5	Over-feed ratio	na	na	1.47	1.47	na	na	1.25
	Hard Yarns wt., g/m <sup>2</sup>	135	135	104	104	205	205	0
	Contractibles wt., g/m <sup>2</sup>	24	24	30	30	0	0	44
	Total wt., g/m <sup>2</sup>	159	159	184	184	314	314	87
	Gathering							
10	Contracted wt., g/m <sup>2</sup>	413	413	537	537	636	636	361
	Contraction ratio	2.6	2.6	2.9	2.9	2.0	2.0	4.15
	Nonwoven wt., g/m <sup>2</sup>	0	0	145	145	0	0	176
	Hard Yarns wt., g/m <sup>2</sup>	351	351	302	302	415	415	na
	Nonwoven total gather	na	na	4.3	4.3	na	na	5.2
15	% of original area	38	38	35	35	49	49	24
	Resin application							
	Resin wt., g/m <sup>2</sup>	646	102	1263	192	1680	560	1020
	% pile height loss	0	0	0	0	0	0	0
	Surface layer characteristics							
20	Total wt., g/m <sup>2</sup>	997	453	1710	639	2095	975	1196
	Thickness, mm	1.1	1.1	2.0	2.0	2.6	2.6	1.1
	Density, g/cm <sup>3</sup>	0.91	0.41	0.86	0.32	0.81	0.38	1.08
	Pile fiber weight g/m <sup>2</sup>	351	351	447	447	415	415	176
	Pile fiber conc g/cm <sup>3</sup>	0.32	0.32	0.22	0.22	0.16	0.16	0.16
25	Eff. pile conc, g/cm <sup>3</sup>	0.32	0.32	0.18	0.18	0.16	0.16	0.08
	Pile Parameter, g/cm <sup>3</sup>	0.54	0.36	0.40	0.24	0.36	0.25	0.29
	Loop base, B, mm	0.7	0.7	0.5	0.5	0.8	0.8	0.4
	Loop H/B ratio	3.6	3.6	5.0	5.0	3.8	3.8	3.5
	Wt. % resin	64	22	74	30	80	57	85
30	% voids	24	66	28	72	32	68	10
	% stretchability	0	20	0	15	0	0	0
	% compressibility	0	15	0	15	0	0	0
	40-grit abrasion resistance							
	Test duration, 10 <sup>3</sup> cycles	13	1.5	25	7.9	25	6	13.2
35	Wear, microns/10 <sup>3</sup> cycles	18	80	25	66	30	60	50
	% Normalized wear*	36	160	50	132	60	120	100

Notes: \* = normalized to Sample E; na = not applicable;

**Example 3**

This example further illustrates the strong effects of total gather and of concentration of pile-like fibers on the abrasion resistance of composite sheets of the invention. Composite sheet Samples 6, 7 and 8 and comparison 5 Sample F each contain a layer in which the pile-like fibers are derived from both a buckled fibrous nonwoven layer and buckled non-elastic stitching yarns. In comparison Sample G, the buckled non-elastic yarns are not present.

To prepare the starting fabric for each sample, a fibrous layer of 26-g/m<sup>2</sup> Sontara® 8017 spunlaced fabric of nonbonded polyester fibers was overfed to a two-bar "Liba" stitchbonding machine. The front bar of the Liba formed a repeating pattern of 1-0,2-3 stitches with combination yarn that was a 280-den (311-dtex) Lycra® spandex elastic core, tightly wound 9 turns/inch (3.5/cm) with 70-den (78-dtex) 34 filament polyester yarn. 10 Except for the fabric of comparison Sample G, which employed no back-bar, the back bar formed a repeating pattern of 3-4, 1-0 stitches with a 210 den (233 dtex) 34 filament high tenacity Type 62 Dacron® polyester yarn. 15 Lycra® and Dacron® are each sold by DuPont. The Liba, a 14-gauge (14 needles per inch or 5.5/cm) machine, inserted 14 courses per inch (5.5/cm). 20 Different amounts of tension were imposed on the combination yarn used to prepare each sample with a different amount of contraction when the fabric was removed from the Liba. The contraction of the combination yarn caused a layer of pile-like fibers to develop. The pile-like fibers were formed by contraction and buckling of the nonwoven fibrous layer and buckling of the 25 back-bar non-elastic stitching yarns, which accompanied the contraction of the combination yarn. Then after boil-off the contracted fabrics were heat treated on the tenter frame to set the final dimensions of the fabric. Thereafter, the fabric samples were impregnated with polyurethane resin PU-1, the same resin as was used in Example 1, to immobilize the pile-like 30 fibers. The impregnated samples were then dried to form the composite sheet sample. Sample details and abrasion test results are summarized in Table III, below.

Table III (Example 3)

Sample Identification		6	7	8	E	G
<b>Starting Materials</b>						
	Nonwoven wt., g/m <sup>2</sup>	26	26	26	26	26
5	Over-feed ratio	1.2	1.2	1.2	1.2	1.3.
	Hard yarns, g/m <sup>2</sup>	71	71	71	71	0
	Contractibles wt., g/m <sup>2</sup>	31	31	31	31	32
	Total wt., g/m <sup>2</sup>	133	133	133	133	66
<b>Gathering</b>						
10	Contracted wt., g/m <sup>2</sup>	578	785	918	238	544
	Contraction ratio	4.4	5.9	6.9	1.8	8.2
	Nonwoven wt., g/m <sup>2</sup>	137	183	215	56	277
	Hard yarn wt. g/m <sup>2</sup>	312	418	490	128	0
	Nonwoven total gather	5.3	7.1	8.3	2.2	10.7
15	% of original area	19	14	15	45	12
	Resin application					
	Resin wt., g/m <sup>2</sup>	1043	884	655	499	986
	% Pile height loss	10	9	15	8	0
<b>Surface layer characteristics</b>						
20	Total wt., g/m <sup>2</sup>	1489	1485	1360	683	1263
	Thickness, mm	1.8	2.0	1.8	1.4	1.6
	Density, g/cm <sup>3</sup>	0.83	0.74	0.75	0.50	0.79
	Pile fiber weight, g/m <sup>2</sup>	449	601	705	184	277
	Pile fiber conc., g/cm <sup>3</sup>	0.25	0.30	0.39	0.13	0.17
25	Eff. pile conc, g/cm <sup>3</sup>	0.21	0.25	0.33	0.11	0.085
	Pile Parameter, p, g/cm <sup>3</sup>	0.41	0.44	0.49	0.23	0.26
	Loop base, B, mm	0.44	0.30	0.25	1.0	0.30
	Loop H/B ratio	4.1	6.6	7.2	1.4	5.3
	% resin	70	60	48	73	78
30	% voids	31	38	38	58	34
	% stretchability	5	5	10	5	0
	% compressibility	10	5	10	15	0
<b>40-grit abrasion resistance</b>						
	Test duration, 10 <sup>3</sup> cycles	23	31	25	2.3	16
35	Wear, microns/10 <sup>3</sup> cycles	32	13	12	80	92
	% normalized wear	35	14	13	87	100

Notes: \*Normalized to Sample G.

Example 4

5 In this example composite sheet samples are prepared from contracted fabric that was single-bar knit with an elastic combination yarn having a loosely wound non-elastic wrapping yarn. The pile-like fibers are formed from the wrapping yarn when the combination yarn contracts.

Samples 9, 10 and 11 and comparison Sample H were each knit with a one-bar "Liba" machine forming a repeating pattern of 1-0,2-3 stitches with a combination yarn that had a 280-den (311-dtex) Lycra® spandex elastic core loosely wrapped at about 1.5 turns/inch (0.6/cm) with a 70-den (78-dtex) 34-filament textured polyester yarn. Each sample was made with the Liba operating at 14 courses/inch (5.5/cm) and the needle bar at 20 gage (i.e., 20 needles per inch or 7.9/cm), except Sample 11 which was made at 10 gage. The fabrics for each sample were knit with the combination yarn under a different tension. Upon removal of the fabric from the knitting machine and 10 tension in the combination yarn was released and the as-knit area of the fabric contracted by a factor 11.5 to 14 times, with an accompanying buckling of the loosely wound wrapping yarn to form the pile-like layer. Polyurethane resin, PU-2, as was used in Example 2, was applied to the pile-like fibers of each sample. Further details of sample fabrication and abrasion 15 performance are listed below in Table IV, which also includes Sample G of Sample 20 Example 3 for further comparison purposes.

The abrasion test results listed in Table IV show that high pile concentrations and high pile parameters and accompanying high abrasion resistance can be obtained with fabrics having pile-like groups of fibers provided by only buckled yarns. The results also demonstrate the importance of avoiding excessive stretchability in the composite sheet. Note that the pile-like fiber/resin surface layer of the composite sheet of comparison Sample H, having a resin content of only 25 weight %, was readily stretchable and exhibited an 11 to 18 times greater abrasion rate than did composite sheet Samples 9-11 of the invention. Unless sufficient resin is incorporated in the fiber/resin layer, even if other characteristics of the layer are in accordance with the invention, the composite sheet will still lack resistance to stretching and abrasion. The abrasion-resistance data and other details of the samples are summarized in Table IV and clearly demonstrate the superior abrasion resistance of the composite sheets of the invention over the comparison samples. The data again show that a resin-impregnated pile-like fiber layer meeting the requirements of the present invention provides a composite sheet with highly effective abrasion resistance.

Table IV (Example 4)

Sample Identification		<u>9</u>	<u>10</u>	<u>11</u>	<u>H</u>	<u>G</u>
<b>Starting Materials</b>						
	Nonwoven wt., g/m <sup>2</sup>	0	0	0	0	26
5	Over-feed ratio	na	na	na	na	1.3.
	Hard yarns, g/m <sup>2</sup>	0	0	0	0	0
	Wrap yarn weight, g/m <sup>2</sup>	24	24	21	24	0
	Contractibles wt., g/m <sup>2</sup>	22	22	20	22	32
	Total wt., g/m <sup>2</sup>	46	46	41	46	66
10 Gathering						
	Contracted wt., g/m <sup>2</sup>	557	557	476	557	544
	Contraction ratio	11.5	11.5	14.0	11.5	8.2
	Nonwoven wt., g/m <sup>2</sup>	0	0	0	0	277
	Nonwoven total gather	na	na	na	na	10.7
15	Wrap yarn wt. g/m <sup>2</sup>	276	276	294	276	0
	% of original area	8.7	8.7	7.8	8.7	12
Resin application						
	Resin wt., g/m <sup>2</sup>	910	1009	987	94	986
	% Pile height loss	17	17	13	17	0
20 Surface layer characteristics						
	Total wt., g/m <sup>2</sup>	1186	1285	1281	370	1263
	Thickness, mm	1.5	1.5	1.4	1.5	1.6
	Density, g/cm <sup>3</sup>	0.79	0.86	0.91	0.25	0.79
	Pile fiber weight, g/m <sup>2</sup>	276	276	294	276	277
25	Pile fiber conc., g/cm <sup>3</sup>	0.18	0.18	0.21	0.18	0.17
	Eff. pile conc., g/cm <sup>3</sup>	0.18	0.18	0.21	0.18	0.085
	Pile Parameter, p, g/cm <sup>3</sup>	0.38	0.38	0.44	0.38	0.26
	Loop base, B, mm	0.12	0.12	0.10	0.12	0.30
	Loop H/B ratio	12.5	12.5	14.0	12.5	5.3
30	% resin	76	78	77	25	78
	% voids	35	28	24	79	34
	% stretchability	10	5	5	80	0
	% compressibility	10	5	10	15	0
40-grit abrasion resistance						
35	Test duration, 10 <sup>3</sup> cycles	20	18	23	0.8	16
	Wear, microns/10 <sup>3</sup> cycles	30	40	43	450	92
	% normalized wear	33	43	47	489	100

Notes: \*Normalized to Sample G.

Example 5

In this example, resin-impregnated composite sheets were prepared from contracted two-bar warp-knit fabrics. The starting fabric for each of Samples 12-15 and Comparison Sample I was knit on a two-bar Liba machine, with one bar threaded with an elastic combination yarn having a loosely wound non-elastic wrapping yarn and the second bar threaded with non-elastic textile yarn. The front bar formed repeating patterns of 1-0,2-3 stitches with a 280-den (311-dtex) Lycra® spandex around which was loosely wound, at one turn/inch (0.4/cm), a 70-den (78-dtex) 34-filament textured polyester yarn. The back bar formed a repeating pattern of 3-4,1-0 stitches with a 150-denier (167-dtex) conventional polyester textile yarn. Each sample was made with the Liba operating at 14 courses/inch (5.5/cm), except Sample 12 and comparison Sample J, which were each made with 22 courses per inch (8.7/cm) and with the machine threaded at 20 gauge, and Sample 13 which was made with the machine threaded at 10 gage. Tension on the combination yarn used to prepare the samples was adjusted so that when the knit fabric was removed from the Liba, boiled-off and heat set, the as-knit area of the fabric contracted by a factor of 1.9 to 7. The contraction of the fabric was accompanied by contraction and buckling of the loosely wound wrapping yarn and buckling of the second bar yarn. Polyurethane PU-2 (same as in Example 2) was applied to each sample.

Further fabrication and abrasion performance details of the samples are summarized in Table V below, in which Sample G of Example 3 is also included for further comparison. The abrasion wear results show that Comparison Samples G and I, exhibited between about 2.5 to about 20 times as much abrasion wear as did Samples 12-15 of the invention. The pile-like fibers of the fabric of Sample I apparently were deflected from the vertical position during application of resin, as indicated by the 31% loss in surface layer height and the insufficient contraction ratio.

The results summarized in Table V showed that contraction of the fabric for Samples 12-15 of the invention resulted in substantially vertical pile-like fibers being formed. The pile-like fibers were derived from both the contracted wrapping yarn and from the buckled second bar yarn. In contrast, the fabrics of comparison Sample I did not provide a satisfactory pile-like layer and was not adequately resin impregnated and accordingly exhibited much inferior abrasion resistance. Sample G, despite its very high resin density did not provide high abrasion resistance because of the low effective pile density and low pile parameter.

Table V (Example 5)

Sample Identification		<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	I	G
<b>Starting Materials</b>							
	Nonwoven wt., g/m <sup>2</sup>	0	0	0	0	0	26
5	Over-feed ratio	na	na	na	na	na	1.3
	Hard yarns wt., g/m <sup>2</sup>	92	32	32	32	92	0
	Wrap yarns wt., g/m <sup>2</sup>	33	23	23	23	26	0
	Contractibles wt., g/m <sup>2</sup>	28	22	22	22	26	32
	Total wt., g/m <sup>2</sup>	153	77	77	77	154	66
10	Gathering						
	Contracted wt., g/m <sup>2</sup>	554	540	870	870	299	544
	Contraction ratio	3.6	7.0	11.3	11.3	1.9	8.2
	Nonwoven wt., g/m <sup>2</sup>	0	0	0	0	0	277
	Hard yarn wt., g/m <sup>2</sup>	331	224	361	361	175	0
	Wrap yarn wt., g/m <sup>2</sup>	118	161	260	260	49	0
	Nonwoven total gather	na	na	na	na	na	10.7
15	% of original area	28	14	9	9	53	12
	Resin application						
	Resin wt., g/m <sup>2</sup>	826	1098	380	920	408	986
20	% pile height loss	16	4	15	0	31	0
	Surface layer characteristics						
	Total wt., g/m <sup>2</sup>	1275	1483	1001	1541	632	1263.
	Thickness, mm	1.6	2.4	1.7	1.9	1.3	1.6
	Density, g/cm <sup>3</sup>	0.65	0.74	0.59	0.81	0.49	0.79
25	Pile fiber weight, g/m <sup>2</sup>	449	385	621	621	224	277
	Pile fiber conc., g/cm <sup>3</sup>	0.28	0.16	0.37	0.33	0.17	0.17
	Eff. pile conc., g/cm <sup>3</sup>	0.28	0.16	0.37	0.33	0.17	0.085
	Pile Parameter, g/cm <sup>3</sup>	0.43	0.34	0.47	0.51	0.28	0.26
	Loop base, B, mm	0.3	0.3	0.2	0.2	0.3	0.3
30	Loop H/B ratio	5.3	8.9	8.5	8.5	4.3	5.3
	Wt. % resin	65	74	38	60	65	78
	% voids	46	38	51	33	59	34
	% stretchability	10	5	10	0	5	0
	% compressibility	10	5	10	0	25	0
35	40-grit abrasion resistance						
	Test duration, 10 <sup>3</sup> cycles >25	>25	>25	>25	>25	4	16
	Wear, microns/10 <sup>3</sup> cycles	28	40	8	5	100	92
	% normalized wear*	30	40	9	5	109	100

Notes: na = not applicable; \* = normalized to sample G

Example 6

In this example, composite sheet samples were prepared which had resin-impregnated fork-needled pile-like fibrous layers.

The starting fabrics for Sample J and 16 were prepared from a 272-g/m<sup>2</sup> air-laid web of 1.5-den (1.7-dtex), 3-inch (7.6-cm) long Type 54 Dacron® polyester fiber (sold by E. I. du Pont de Nemours & Co.) that was placed upon and fork needled into a 119-g/m<sup>2</sup> Reemay® spunbonded polyester fabric with a Dilo fork needler. The needler was a 14 gauge (14 fork needles per inch or 5.5/cm) machine that made about 130 insertions square inch (20/cm<sup>2</sup>). Loops of fiber were formed on the surface of the Reemay® that was opposite to the side the needles entered the layer. The loops projected about 2.5 mm above the surface of the Reemay®. Comparison Sample J was boiled off, heat set, impregnated with polyurethane, PU-2 and then dried. Sample 16 was treated the same way, except that prior to the heat-setting, resin-impregnation and drying, Sample 16 was stretched longitudinally by 30% with a corresponding decrease to about 37% of its original width to provide the sample with a contraction in area by a factor of 2.1. Further fabrication details, characteristics of the samples and abrasion wear test results are summarized in Table VI. The summary also includes data for comparison Sample G of Example 3 for further comparison purposes.

Table VI clearly shows that composite sheet Sample 16 of the invention, containing a pile-like fiber layer prepared by fork-needling and contraction, is 6.5 times as abrasion resistant as a similarly prepared composite sheet having fork-needled pile-like layer that was not contracted. Also, the composite sheet of Sample 16 was 4.5 times as abrasion resistant as the composite sheet of comparison Sample G of Example 3. These results, emphasize, as was shown in the preceding examples as well, that the pile parameter of the resin-impregnated pile-fiber layer is very important in providing a composite sheet with abrasion resistance. Sample 16 of the invention had a pile parameter of 0.37, while comparison Sample J and G respectively had pile parameters of 0.22 and 0.26.

TABLE VI (Example 6)

Sample Identification		J	16	G
<b>Starting Materials</b>				
	Nonwov n wt., g/m <sup>2</sup>	272	272	26
5	Over-feed ratio	na	na	1.3
	Contractibles wt., g/m <sup>2</sup>	119	119	32
	Total wt., g/m <sup>2</sup>	391	391	66
<b>Gathering</b>				
	Contracted wt., g/m <sup>2</sup>	391	821	544
10	Contraction ratio	1.0	2.1	8.2
	Nonwoven wt., g/m <sup>2</sup>	272	571	277
	Nonwoven total gather	1.0	2.1	10.7
	% of original area	100	48	12
<b>Resin application</b>				
15	Resin wt., g/m <sup>2</sup>	720	930	986
	% pile height loss	0	0	0
<b>Surface layer characteristics</b>				
	Total wt., g/m <sup>2</sup>	992	1501	1263
	Thickness, mm	2.4	2.5	1.6
20	Density, g/cm <sup>3</sup>	0.41	0.60	0.79
	Pile fiber weight, g/m <sup>2</sup>	272	571	277
	Pile fiber conc., g/cm <sup>3</sup>	0.11	0.23	0.17
	Eff. pile conc., g/cm <sup>3</sup>	0.11	0.23	0.085
	Pile Parameter, g/cm <sup>3</sup>	0.22	0.37	0.26
25	Loop base, B, mm	0.8	0.4	0.3
	Loop H/B ratio	3.0	6.0	5.3
	Wt. % resin	73	62	78
	% voids	65	50	34
	% stretchability	10	0	0
30	% compressibility	15	0	0
<b>40-grit abrasion resistance</b>				
	Test duration, 10 <sup>3</sup> cycles	5	15	16
	Wear, microns/10 <sup>3</sup> cycles	130	20	92
	% normalized wear*	141	22	100
35	<u>Notes:</u> na = not applicable; * = normalized to sample G			

**Example 7**

In this example, two composite sheet samples were prepared with resin-impregnated velour fabrics providing the pile-like fibers for the resin/fiber layers.

5       The starting fabrics for Sample 17 and 18 were prepared on a 130-inch (3.3-meter) wide, 70 gauge (70 needles/inch or 27.6/cm), three-bar warp-knitting machine which formed 64 course per inch (25.2/cm). A type KS3P machine, manufactured by Karl Mayer of Frankfurt, Germany, was used. The first bar was threaded with a flat (i.e., not textured) 70-den (77-dtex), 24-filament polyester yarn and formed a repeating pattern of 1-0, 1-1, 10 2-1 stitches. The second bar was threaded with a flat, 100-den (110-dtex) 40-filament polyester yarn and formed a repeating pattern of 1-0, 0-0, 1-1 stitches. The third bar was threaded with a flat (i.e., not textured) 70-den (77-dtex), 24-filament polyester yarn and formed a repeating pattern of 1-0, 15 0-0, 1-1 stitches. The velour fabric that was formed by the machine had a knit backing (i.e., base) layer that weighed 347 g/m<sup>2</sup> and layer of looped yarns that measured 1.5 mm high, weighed 231 g/m<sup>2</sup>, had a effective pile fiber concentration of 0.18 g/cm<sup>3</sup>.

20      Sample 17, in the as-knitted condition, was impregnated with polyurethane resin PU-2. After resin curing, the sample had a pile parameter of 0.31 g/cm<sup>3</sup>. Sample 18, in the as-knit condition, was heat set at a temperature of 375°F (191°C) to stabilize the fabric dimensions. Then the loops of the heat-set Sample 18 were sheared to provide a pile thickness of 1.2 mm. Sample 18 also was impregnated with polyurethane resin PU-2, 25 which after curing also provided the sample with a pile parameter of 0.31 g/cm<sup>3</sup>.

As shown in Table VII, Samples 17 and 18 were composite sheets of the invention that performed quite well in the 40-grit abrasion wear test. Comparison Sample G of Example 3 was also included in the Table VII for further comparison. As compared to the composite sheets of Samples 17 and 18 of the invention with their resin-impregnated velour fabrics, the composite sheet of comparison Sample G with its resin-impregnated contracted-and-buckled nonwoven fibrous layer abraded 2.2 to 2.4 times as rapidly as Samples 17 and 18.

TABLE VII (Example 7)

Sample Identification		17	18	G
<b>Starting Materials</b>				
	Base layer weight, g/m <sup>2</sup>	347	347	na
5	Pile weight, g/m <sup>2</sup>	231	231	na
	Pile height, mm	1.5	1.5	na
<b>After heat setting &amp; shearing*</b>				
	Base layer weight, g/m <sup>2</sup>	347	347	na
	Pile weight, g/m <sup>2</sup>	231	210	na
10	Pile height, mm	1.5	1.4	na
<b>Resin application</b>				
	Resin weight, g/m <sup>2</sup>	452	422	986
	% pile height loss	15	15	0
<b>Surface layer characteristics</b>				
15	Total weight, g/m <sup>2</sup>	683	682	1263
	Thickness, mm	1.3	1.2	1.6
	Density, g/cm <sup>3</sup>	0.53	0.53	0.79
	Pile fiber weight, g/m <sup>2</sup>	231	210	277
	Pile fiber conc., g/cm <sup>3</sup>	0.18	0.18	0.17
20	Eff. pile conc., g/cm <sup>3</sup>	0.18	0.18	0.085
	Pile Parameter, g/cm <sup>3</sup>	0.31	0.31	0.26
	Base, B, mm	0.4	0.4	0.3
	H/B ratio	3.3	3.0	5.3
	Wt. % resin	66	67	78
25	% voids	45	44	34
	% stretchability	10	0	0
	% compressibility	15	15	0
<b>40-grit abrasion resistance</b>				
	Test duration, 10 <sup>3</sup> cycles	16	15	16
30	Wear, microns/10 <sup>3</sup> cycles	41	38	92
	% normalized wear*	45	41	100

Notes: \* Only Sample 18 was sheared. "na" means not applicable,

See Table III (Example 3) for further details about Sample G.

\* % wear normalized to Sample G.

**I CLAIM:**

1. An abrasion-resistant composite sheet having an upper surface and a lower surface and including
  - 5 a planar fibrous network located between and substantially parallel to the upper and lower surfaces,
  - groups of pile-like fibers located between the lower and upper surfaces of the sheet, being connected to and protruding generally perpendicularly from the planar fibrous network,
  - 10 a resin immobilizing the pile-like groups of fibers in the generally perpendicular position and amounting to in the range of 30 to 90 % of the total weight of the resin-impregnated pile layer ,
  - the groups of pile-like fibers and the planar fibrous network being composed of fibers or filaments of textile decitex, and
  - 15 the sheet having a stretchability of no greater than 25% in any direction,
  - characterized by, in combination,
  - the groups of pile-like fibers being present in the resin-impregnated pile-like fiber layer in an effective pile fiber concentration,  $c_{eff}$ , of at least 0.1 g/cm<sup>3</sup>, and
  - 20 the resin-impregnated pile-like layer having a thickness in the range of 0.5 to 3 mm, an over-all density, d, of at least 0.4 g/cm<sup>3</sup>, a unit weight in the range of 300 to 2,500 g/m<sup>2</sup>, a vertical compressibility of no greater than 25% and a pile parameter P, calculated by the equation,  $P = [(c_{eff})(d)]^{1/2}$ , of at least 0.3 g/cm<sup>3</sup>.
- 25 2. A composite sheet of claim 1 wherein the resin amounts to at least 50% of the total weight of the resin-impregnated pile-like fiber layer, the effective pile fiber concentration is in the range of 0.15 to 0.5 g/cm<sup>3</sup>, the layer thickness is in the range of 1 to 3 mm, the over-all density of the layer is in the range of 0.5 to 1.2 g/cm<sup>3</sup>, the pile parameter is at least 0.35 g/cm<sup>3</sup>, and the layer exhibits a 40-grit Wyzenbeek abrasion wear of no more than 50 microns per 1000 cycles.
- 30 3 A composite sheet of claim 1 or 2 wherein the stretchability of the composite sheet and the compressibility of the resin-impregnated pile-like layer are each no greater than 10%.
- 35 4. A composite sheet of claim 1, 2 or 3 wherein the groups of pile-like fibers are in the form of inverted U-shaped loops or vertical yarns having an average spacing in the range of 0.1 to 2 mm and an average loop height-to-base ratio of at least 0.5, said loops being formed by buckled yarns

and the planar fibrous network is provided at least in part by contracted yarns.

5. A composite sheet of claim 4 wherein the planar fibrous network is a knit fabric comprising a combination yarn having a contracted core and a buckled hard yarn wrapping, the buckled wrapping forming groups of pile-like fibers.

10. 6. A composite sheet of claim 4 wherein the planar fibrous network is a knit fabric formed with at least two bars, one bar providing a combination yarn with a contracted core and a second bar providing a hard yarn which is buckled to form the groups of pile-like fibers.

7. A composite sheet of claim 4 wherein the planar fibrous layer comprises a nonwoven fabric of fibers or filaments of textile decitex and the groups of pile-like fibers are tufted yarns.

15. 8. A composite sheet of claim 4 wherein the planar fibrous layer comprises a contracted knit fabric and the groups of pile-like fibers are tufted yarns.

9. A composite sheet of claim 4 wherein the U-shaped loops are formed in part from a contracted nonwoven layer of substantially nonbonded fibers of textile decitex.

20. 10. A composite sheet of claim 4 wherein the planar fibrous layer is a stitchbonded fibrous layer, wherein the stitchbonding yarn is a combination yarn having a contractile core and a loosely wrapped hard yarn wrapping.

25. 11. A composite sheet of claim 4 wherein the planar fibrous layer and the groups of pile-like fibers are both provided from a contracted two-bar stitchbonded fibrous layer, wherein the stitchbonding yarn of one bar is a combination yarn with a contractile core and the stitchbonding yarn of the second bar is a hard yarn.

30. 12. A composite sheet of claim 1, 2 or 3 wherein the pile fibers and the planar fibrous network are provided by a velour fabric.

13. A process for making an abrasion-resistant composite sheet comprising the steps of

35. providing a fabric having a thickness of 0.5 to 3 mm within which groups of pile-like fibers are generally perpendicular to the surface of the fabric and are present in an effective pile-fiber concentration of at least 0.1 gram/cm<sup>3</sup> and the groups of pile-like fibers are connected to and protruding from a planar fibrous network located in or at a surface of the surface of the fabric, and

immobilizing the groups of pile-like fibers in their perpendicular position by incorporating resin into the fabric in an amount that constitutes in the range of 30 to 90% of the total weight of the impregnated fabric and provides the impregnated fabric with an over-all density of in the range of 5 0.4 to 1.2 g/cm<sup>3</sup>, and a pile parameter of at least 0.3 g/cm<sup>3</sup>.

14. A process of claim 10 wherein the concentration of the groups of pile-like fibers is increased by contracting the area of the fabric by a factor of at least 2.

15. A process of claim 11 wherein the fabric is contracted by a 10 factor in the range of 3 to 12.

16. A process of claim 11 or 12 wherein the fabric is knit 15 fabric that was knitted with combination yarns under tension, and optionally with hard yarns, the combination yarns having an elastic core combined with a filamentary wrapping and forming knit stitches that provide intervals of at least 1-mm length and the tension being released in the contraction step.

17. A process in accordance with claim 10 wherein the immobilization of the groups of pile-like fibers and the stabilization of the dimensions of the fabric are accomplished simultaneously by the incorporation of the resin.

18. A process in accordance with claim 14 wherein the 20 composite sheet is further stabilized by attaching elements of low stretch to the back of the composite sheet.

19. A shaped article having attached to at least a portion of a 25 surface thereof, an abrasion-resistant composite sheet in accordance with claim 1.

**AMENDED CLAIMS**

[received by the International Bureau on 25 July 1995 (25.07.95);  
original claims 3, 14, 15, 16, 17 and 18 amended;  
remaining claims unchanged (3 pages)]

1. An abrasion-resistant composite sheet having an upper surface and a lower surface and including
  - 5      a planar fibrous network located between and substantially parallel to the upper and lower surfaces,
    - 10      groups of pile-like fibers located between the lower and upper surfaces of the sheet, being connected to and protruding generally perpendicularly from the planar fibrous network,
    - 15      a resin immobilizing the pile-like groups of fibers in the generally perpendicular position and amounting to in the range of 30 to 90 % of the total weight of the resin-impregnated pile layer,
    - 20      the groups of pile-like fibers and the planar fibrous network being composed of fibers or filaments of textile decitex, and
    - 25      the sheet having a stretchability of no greater than 25% in any direction,
  - 30      characterized by, in combination,
    - 35      the groups of pile-like fibers being present in the resin-impregnated pile-like fiber layer in an effective pile fiber concentration,  $c_{eff}$ , of at least  $0.1 \text{ g/cm}^3$ , and
    - 40      the resin-impregnated pile-like layer having a thickness in the range of 0.5 to 3 mm, an over-all density,  $d$ , of at least  $0.4 \text{ g/cm}^3$ , a unit weight in the range of 300 to  $2,500 \text{ g/m}^2$ , a vertical compressibility of no greater than 25% and a pile parameter  $P$ , calculated by the equation,  $P = [(c_{eff})(d)]^{1/2}$ , of at least  $0.3 \text{ g/cm}^3$ .
  - 45      2. A composite sheet of claim 1 wherein the resin amounts to at least 50% of the total weight of the resin-impregnated pile-like fiber layer, the effective pile fiber concentration is in the range of  $0.15$  to  $0.5 \text{ g/cm}^3$ , the layer thickness is in the range of 1 to 3 mm, the over-all density of the layer is in the range of  $0.5$  to  $1.2 \text{ g/cm}^3$ , the pile parameter is at least  $0.35 \text{ g/cm}^3$ , and the layer exhibits a 40-grit Wyzenbeek abrasion wear of no more than 50 microns per 1000 cycles.
  - 50      3. A composite sheet of claim 2 wherein the stretchability of the composite sheet and the compressibility of the resin-impregnated pile-like layer are each no greater than 10%.
  - 55      4. A composite sheet of claim 1, 2 or 3 wherein the groups of pile-like fibers are in the form of inverted U-shaped loops or vertical yarns having an average spacing in the range of 0.1 to 2 mm and an average loop height-to-base ratio of at least 0.5, said loops being formed by buckled yarns

and the planar fibrous network is provided at least in part by contracted yarns.

5. A composite sheet of claim 4 wherein the planar fibrous network is a knit fabric comprising a combination yarn having a contracted core and a buckled hard yarn wrapping, the buckled wrapping forming groups of pile-like fibers.

10 6. A composite sheet of claim 4 wherein the planar fibrous network is a knit fabric formed with at least two bars, one bar providing a combination yarn with a contracted core and a second bar providing a hard yarn which is buckled to form the groups of pile-like fibers.

7. A composite sheet of claim 4 wherein the planar fibrous layer comprises a nonwoven fabric of fibers or filaments of textile decitex and the groups of pile-like fibers are tufted yarns.

15 8. A composite sheet of claim 4 wherein the planar fibrous layer comprises a contracted knit fabric and the groups of pile-like fibers are tufted yarns.

9. A composite sheet of claim 4 wherein the U-shaped loops are formed in part from a contracted nonwoven layer of substantially nonbonded fibers of textile decitex.

20 10. A composite sheet of claim 4 wherein the planar fibrous layer is a stitchbonded fibrous layer, wherein the stitchbonding yarn is a combination yarn having a contractile core and a loosely wrapped hard yarn wrapping.

25 11. A composite sheet of claim 4 wherein the planar fibrous layer and the groups of pile-like fibers are both provided from a contracted two-bar stitchbonded fibrous layer, wherein the stitchbonding yarn of one bar is a combination yarn with a contractile core and the stitchbonding yarn of the second bar is a hard yarn.

30 12. A composite sheet of claim 1, 2 or 3 wherein the pile fibers and the planar fibrous network are provided by a velour fabric.

13. A process for making an abrasion-resistant composite sheet comprising the steps of

35 providing a fabric having a thickness of 0.5 to 3 mm within which groups of pile-like fibers are generally perpendicular to the surface of the fabric and are present in an effective pile-fiber concentration of at least 0.1 gram/cm<sup>3</sup> and the groups of pile-like fibers are connected to and protruding from a planar fibrous network located in or at a surface of the surface of the fabric, and

immobilizing the groups of pile-like fibers in their perpendicular position by incorporating resin into the fabric in an amount that constitutes in the range of 30 to 90% of the total weight of the impregnated fabric and provides the impregnated fabric with an over-all density of in the range of 5 0.4 to 1.2 g/cm<sup>3</sup>, and a pile parameter of at least 0.3 g/cm<sup>3</sup>.

14. A process of claim 13 wherein the concentration of the groups of pile-like fibers is increased by contracting the area of the fabric by a factor of at least 2.

15. A process of claim 14 wherein the fabric is contracted by a 10 factor in the range of 3 to 12.

16. A process of claim 14 or 15 wherein the fabric is knit 15 fabric that was knitted with combination yarns under tension, and optionally with hard yarns, the combination yarns having an elastic core combined with a filamentary wrapping and forming knit stitches that provide intervals of at least 1-mm length and the tension being released in the contraction step.

17. A process in accordance with claim 13 wherein the immobilization of the groups of pile-like fibers and the stabilization of the dimensions of the fabric are accomplished simultaneously by the incorporation of the resin.

18. A process in accordance with claim 17 wherein the composite sheet is further stabilized by attaching elements of low stretch to the back of the composite sheet.

19. A shaped article having attached to at least a portion of a 25 surface thereof, an abrasion-resistant composite sheet in accordance with claim 1.

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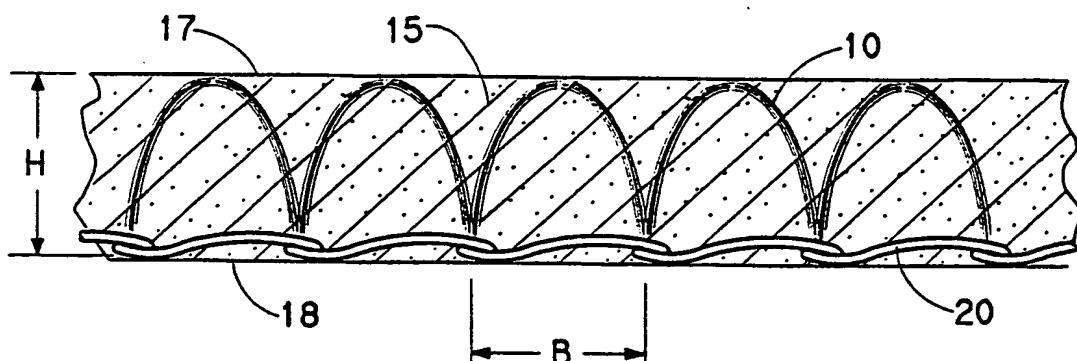


FIG. 1

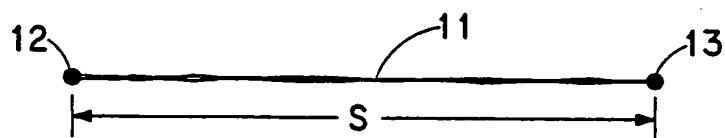


FIG. 2

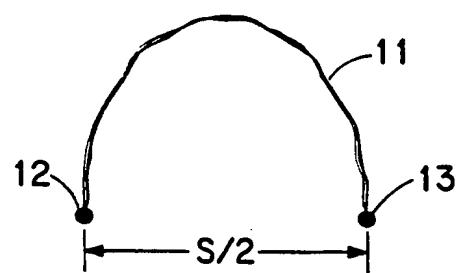


FIG. 3

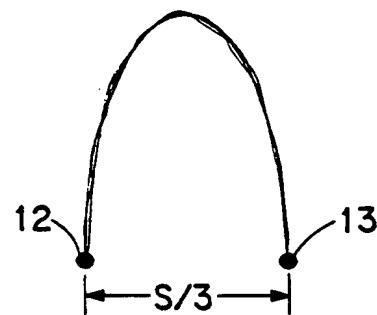


FIG. 4

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/05805

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B32B 3/00, 33/00

US CL :428/86, 96

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/86, 96

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,271,982 (VERPOEST et al.) 21 December 1993, see Figures 3 & 4 and columns 1-4.	1-3, 13 & 19
X	US, A, 4,888,228 (SIDLES) 19 December 1989, see Figures 2 & 3 and columns 1-2.	1-3, 13 & 19
X	US, A, 4,239,829 (COHEN) 16 December 1980, see Figure 4 and column 2, lines 52-61.	1-3, 13 & 19
X	US, A, 3,951,718 (GONZALEZ) 20 April 1976, see Figures 1, 4, & 5 and the Abstract.	1-3, 13 & 19
X	WO, A, WO 94/00043 (TAC-FAST SYSTEMS CANADA LIMITED) 06 January 1994, see Figure 2 and page 9.	1-3, 13 & 19

 Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	&	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

21 JUNE 1995

Date of mailing of the international search report

10 JUL 1995

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Form PCT/ISA/210 (second sheet)(July 1992)★

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/05805

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 2 096 536 (TOYO BOSEKI KABUSHIKI KAISHA) 20 October 1982, see Figure 2, and pages 1-3.	1-3, 13 & 19
A	US, A, 4,159,361 (SCHUPACK) 26 June 1979, see entire document.	1-3, 13 & 19
A	US, A, 3,274,046 (SHANNON et al.) 20 September 1966, see entire document.	1-3, 13 & 19

Form PCT/ISA/210 (continuation of second sheet)(July 1992)\*

**INTERNATIONAL SEARCH REPORT**International application No.  
PCT/US95/05805**B x I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 4-12 & 14-18 because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**  

The additional search fees were accompanied by the applicant's protest.

N protest accompanied the payment of additional search fees.

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